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Process Temperature Dependence of Al_2O_3 Film Deposited by Thermal ALD as a Passivation Layer for c-Si Solar Cells

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Abstract—**This paper presents a study of the process temperature dependence of Al_2O_3 film grown by thermal atomic layer deposition (ALD) as a passivation layer in the crystalline Si (c-Si) solar cells. The deposition rate of Al_2O_3 film maintained almost the same until 250 °C, but decreased from 300 °C. Al_2O_3 film deposited at 250 °C was found to have the highest negative fixed oxide charge density (Q_f) due to its O-rich condition and low hydroxyl group (-OH) density. After post-metallization annealing (PMA), Al_2O_3 film deposited at 250 °C had the lowest slow and fast interface trap density. Actually, Al_2O_3 film deposited at 250 °C showed the best passivation effects, that is, the highest excess carrier lifetime (τ_{PCD}) and lowest surface recombination velocity (S_{eff}) than other conditions. Therefore, Al_2O_3 film deposited at 250 °C exhibited excellent chemical and field-effect passivation properties for p-type c-Si solar cells.**

Index Terms—**Solar cell, Al_2O_3, passivation layer, thermal ALD, negative fixed oxide charge**

I. INTRODUCTION

For high efficient c-Si solar cells, minimizing electrical losses at the surface of the Si has become important because of the trend toward thinner c-Si wafers used as base material [1, 2]. To reduce electrical losses at the surface of Si, two passivation methods can be used [2-4]. The first method is to reduce the defect states at the surface of the Si (i.e., chemical passivation). Because the recombination rate is proportional to the interface defect density, electrical losses can be mitigated by passivating the Si dangling bonds. The second one is to reduce the minority carrier concentration near the surface by a built-in electric field (i.e., field-effect passivation). Because recombination process needs both electrons and holes, the recombination rate can be decreased by reducing the minority carriers near the surface.

For the passivation layer of the p-type c-Si solar cell, many kinds of materials such as SiO_2, a-Si, a-SiN_x, and a-SiC_x had been used [1, 2]. Recently, Al_2O_3 film grown by ALD has attracted strong interest as a passivation layer on p-type c-Si. Due to its high level of negative fixed oxide charge density, Q_f, it can reduce electron concentration near the surface of p-type Si wafer by a built-in electric field. Hence, Al_2O_3 film can suppress the electrical loss by accomplishing both chemical and field-effect passivation on p-type c-Si surfaces [1-4]. However, few studies have addressed the dependence of the passivation characteristics on the process temperature of Al_2O_3 film grown by thermal ALD.

In this work, the dependence of passivation characteristics of thermal ALD Al_2O_3 film on the deposition temperature was investigated in depth for c-Si solar cell.

II. EXPERIMENTAL

The experimental process flow for this work is summarized in Fig. 1. A p-type Si substrate was treated

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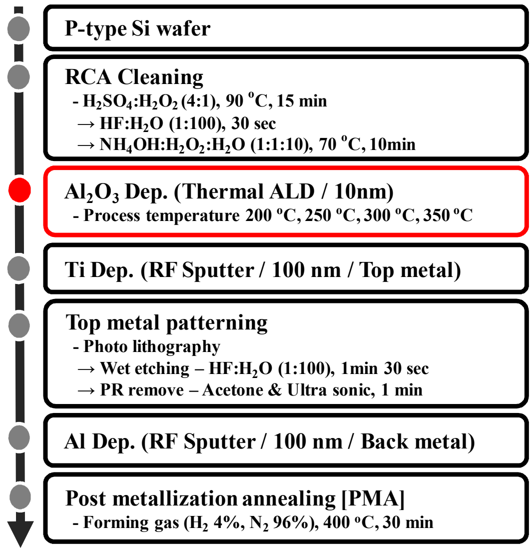


Fig. 1. Process flow for the experiments.

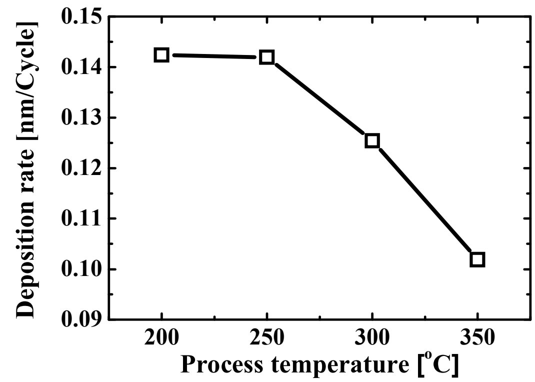


Fig. 2. Deposition rate of Al_2O_3 film as a function of process temperature.

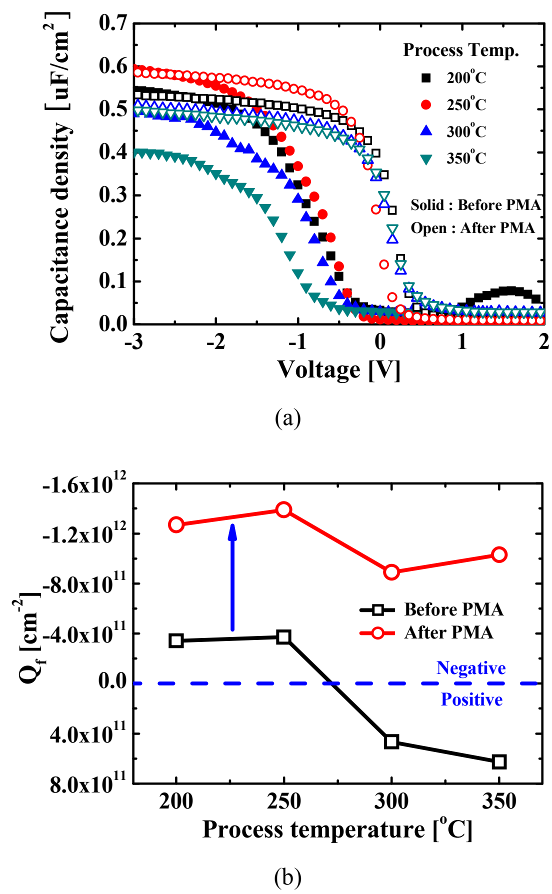


Fig. 3. (a) C-V characteristics of an Al_2O_3 MIS capacitor, (b) Fixed oxide charge density, Q_f of an Al_2O_3 MIS capacitor as a function of process temperature before and after PMA.

with RCA cleaning. Al_2O_3 film (10 nm) was deposited by thermal ALD considering the deposition rate. Ti film (100 nm) was deposited as a top electrode on the Al_2O_3 film by RF magnetron sputtering. After patterning the top metal by photolithography and wet etching, Al film (100 nm) was deposited on the backside of the substrate by RF magnetron sputtering. Finally, post-metallization annealing (PMA) was carried out in a furnace with a forming gas ambient at 400 °C for 30 min.

Thickness of Al_2O_3 film was confirmed by ellipsometry measurement. High frequency capacitance (C_{HF}) and quasi-static capacitance (C_{QS}) were measured using an Agilent 4284A precision LCR meter and an Agilent 4156C semiconductor parameter analyzer, respectively. Al_2O_3 film deposited at different process temperatures was analyzed by X-ray photoelectron spectroscopy (XPS). The depth profile of Al_2O_3 film before and after PMA was investigated by secondary ion mass spectrometry (SIMS). To confirm the passivation properties of Al_2O_3 film deposited at different temperature conditions, Quasi-Steady-State Photoconductance (QSSPC) measurement was carried out.

III. Results and Discussions

As shown Fig. 2, the deposition rate of Al_2O_3 film was about 0.14 nm/cycle at the process temperature from 200 °C to 250 °C. But it began to decrease from 300 °C condition. Due to the process temperature dependence of deposition rate of Al_2O_3 film, the low process temperature (200 ~ 250°C) is more suitable than the high process temperature (300 ~ 350 °C) in terms of process efficiency of c-Si solar cell.

Fig. 3(a) shows the capacitance-voltage (C-V) characteristics of an Al_2O_3 MIS capacitor at 100 kHz. The flatband voltage (V_{FB}) moved toward the positive bias up to 250 °C, but then shifted toward the negative bias from 300 °C before PMA. After PMA, the V_{FB} of all process temperatures shifted abruptly toward the positive bias and appeared to have the same values regardless of process temperature. Fig. 3(b) shows Q_f as a function of process temperature. To extract Q_f, a reference V_{FB}, that is, -1.45 V (before PMA) or -0.53 V (after PMA) calculated from the dependence of V_{FB} on Al_2O_3 thickness was used. Before PMA, Q_f becomes negative only at 200~250 °C, with the highest negative Q_f at 250 °C condition. After PMA, however, Q_f of Al_2O_3 film was negative for all temperature conditions and it became the greatest at 250 °C condition.

Figs. 4(a) and (b) show the hysteresis characteristics of MIS capacitors before and after PMA. Slow interface trap density (N_{si}) was extracted from $\triangle V_{FB}$ in Fig. 4(c). Before PMA, N_{si} decreased as the process temperature increased. After PMA, however, N_{si} decreased for all temperatures with the lowest N_{si} at 250 °C condition.

To confirm the trend of fast interface trap density (D_{it}) through the process temperatures, quasi-static capacitance voltage (QSCV) measurement was performed for the Al_2O_3 MIS capacitor with PMA. From the QSCV curve, the surface potential as a function of voltage was extracted by Berglund's integral [5] and D_{it} was calculated with C_{HF} and C_{QS} from equation (1) [5]:

$$D_{it} = \frac{C_{QS} - C_{HF}}{q}\left(1 - \frac{C_{QS}}{C_{OX}}\right)^{-1}\left(1 - \frac{C_{HF}}{C_{OX}}\right)^{-1} \quad (1)$$

To investigate D_{it} as a function of surface potential, D_{it} was plotted as a function of $E\text{-}E_v$ as shown in Fig. 5(a). The lowest D_{it} distribution was shown at 250 °C and the same D_{it} distribution was seen at other process temperatures. In Fig. 5(b), the lowest midgap D_{it} was seen at 250 °C condition.

The origin of the negative Q_f at 200~250 °C before PMA was identified by XPS analysis. Fig. 6 shows the atomic percentage of the Al2p and O1s peaks of the Al_2O_3 film. In amorphous Al_2O_3, Al vacancies and O interstitials form oxygen dangling bonds (O DBs), which contribute to negative Q_f [6, 7]. In Fig. 6, Al_2O_3 films grown at 200~250°C with a negative Q_f have a higher percentage of O1s and less of Al2p than films deposited

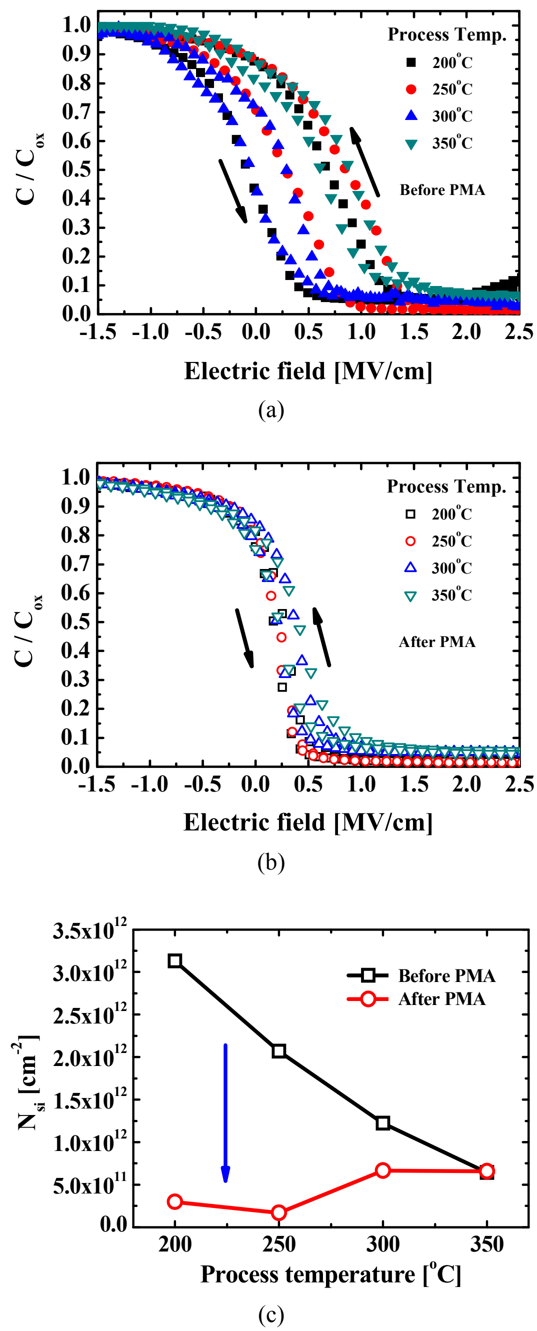
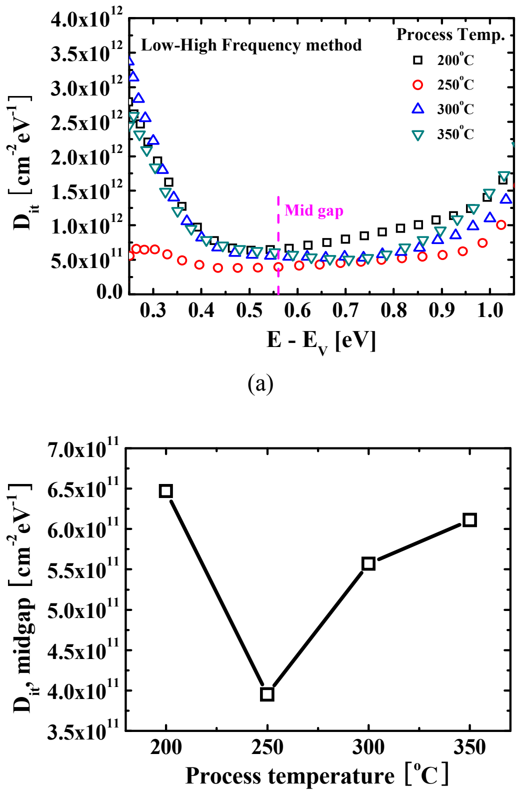


Fig. 4. The hysteresis of an Al_2O_3 MIS capacitor (a) before, (b) after PMA, (c) Slow interface trap density, N_{si} of Al_2O_3 MIS capacitor as a function of process temperature.

at other temperatures. That is, the negative Q_f at 200~250 °C might result from Al vacancies or O interstitials.

Figs. 7(a) and (b) show the O1s peaks at 200~250 °C before PMA, and Fig. 7(c) is the -OH peak (532.6 eV) [9] in the O1s peaks for the 200~250°C conditions before PMA. The –OH peak at 250°C is lower than that at 200°C. O-H bonds occur in the neutral charge state [6],



(a)

(b)

Fig. 5. (a) Fast interface trap density, D_{it} as a function of surface potential after PMA, (b) fast interface trap density D_{it} at midgap as a function of process temperature after PMA.

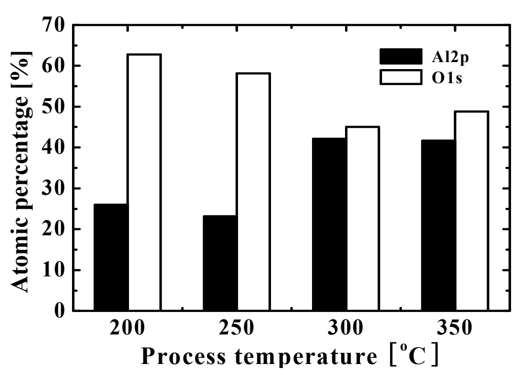
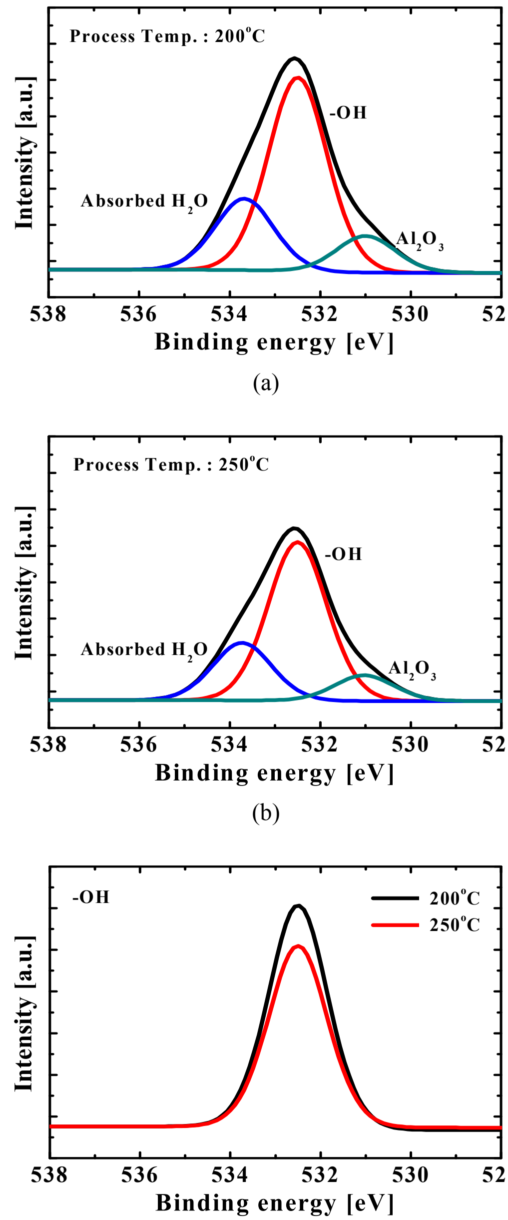


Fig. 6. The atomic percentage of Al2p and O1s peak of as grown Al_2O_3 film.



(a)

(b)

(c)

Fig. 7. Analysis of O1s of as grown Al_2O_3 film (a) at 200 °C, (b) at 250 °C, (c) Comparison of hydroxyl group peak at 200 °C and 250 °C.

and the decrease of the –OH peak indicates the relative increase of O DBs. This, therefore, can explain why the negative Q_f at 250 °C is greater than that at 200 °C.

Fig. 8 shows SIMS profile of the Al_2O_3 film deposited at 250 °C before and after forming gas annealing (FGA). H ions in the Al_2O_3 film diffuse to the interface between Al_2O_3 and Si after annealing, where the H^+ ions passivate N_{si} by mitigating the dangling bonds at the interface of Al_2O_3 and Si substrate [7, 8]. O ions near the interface increase, and O DBs might also increase after annealing. This could explain why the negative Q_f increases after PMA [6, 7].

Fig. 9 exhibits the QSSPC measurement results. Surface recombination velocity, S_{eff} was extracted from equation (2) with excess carrier lifetime, τ_{PCD} which is the result of QSSPC measurement [10, 11].

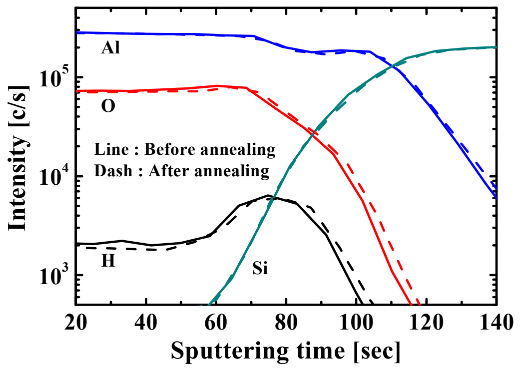


Fig. 8. SIMS profile of Al_2O_3 film at the process temperature of 250 °C.

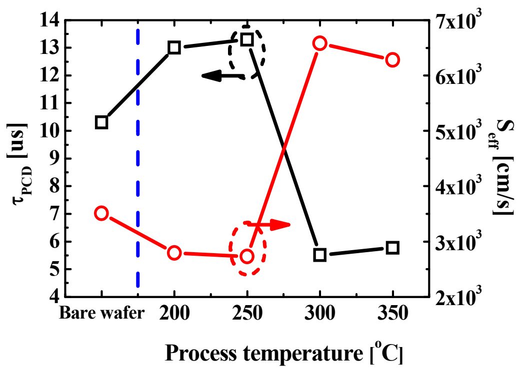


Fig. 9. Excess carrier lifetime and surface recombination velocity of Si wafers deposited with Al_2O_3 at different temperature conditions.

$$\frac{1}{\tau_{PCD}} = \frac{1}{\tau_b} + \frac{2S_{eff}}{W} \quad (2)$$

W is the effective wafer thickness and τ_b is the bulk minority carrier lifetime which is usually assumed to be infinite as the best case.

The highest τ_{PCD} and lowest S_{eff} happened at 250 °C condition. At the high process temperature condition (300 ~ 350 °C), however, τ_{PCD} and S_{eff} became worse than the case without Al_2O_3 passivation layer. Because τ_{PCD} and S_{eff} of Si wafer is closely related with passivation properties of Al_2O_3 film, it can be said that Al_2O_3 film deposited at 250 °C condition has the best passivation effects, that is, possibly the highest efficiency of c-Si solar cell, due to the outstanding chemical and field-effect passivation properties caused by its higher negative Q_f, lower N_{si}, and lower D_{it} than those at other conditions.

V. Conclusions

The process temperature dependence of Al_2O_3 film grown by thermal ALD as a passivation layer in c-Si solar cells was studied. Due to abrupt decrease of the deposition rate of Al_2O_3 film over 300 °C, the low process temperature is more suitable in terms of process efficiency. Because Al_2O_3 film exhibited the highest negative Q_f at 250 °C, it is likely to have outstanding field-effect passivation properties in p-type c-Si at that temperature. XPS analysis showed that Al_2O_3 film at 250 °C before PMA has an O-rich condition and low –OH group density, that is, it had the highest negative Q_f due to great oxygen dangling bonds. At a deposition temperature of 250 °C, Al_2O_3 film also had not only the lowest N_{si} but also the lowest D_{it} after PMA which suggest that Al_2O_3 film deposited at 250 °C will be an excellent chemical passivation layer. From the SIMS profile, FGA made H^+ ions passivate the dangling bonds at the interface between Al_2O_3 and Si substrate. Because FGA also makes Al_2O_3 near the interface more O-rich, the negative Q_f increases by FGA. The highest τ_{PCD} and lowest S_{eff} were appeared at the 250 °C condition likely due to its higher negative Q_f, lower N_{si}, and lower D_{it} than those at other conditions. But τ_{PCD} and S_{eff} are deteriorated from 300 °C. These trends of τ_{PCD} and S_{eff} can be explained by the transition of negative Q_f and interface trap density as chemical and field-effect passivation mechanisms. Therefore, it can be said that Al_2O_3 film deposited at 250 °C demonstrates outstanding promise as a passivation layer due to the concurrent chemical and field-effect passivation effect.

Acknowledgments

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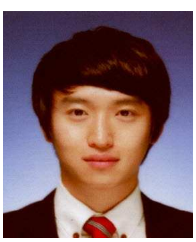

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